

Geochemical evidence (C, N and Pb isotopes) of recent anthropogenic impact in south-central Chile from two environmentally distinct lake sediment records

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ABSTRACT: In this paper, we compare the elemental and isotopic (C, N, Pb) geochemistry of lake sediments from two contrasted environments in south-central Chile. The first lake, Laguna Chica de San Pedro (LCSP), is situated in the urbanised area of the Biobio Region (36°S). The second lake, Lago Puyehue (40°S), is located 400 km to the southeast of LCSP and within an Andean national park. Our aim is to identify environmental impacts associated with increasing industrial activities and land degradation during the last 150 years. In LCSP, shifts in C/N atomic ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ from 1915–1937 to the late 1980s are attributed to successive land degradation episodes in the lake watershed. Based on a Pb isotopic mixing model, we estimate that up to 20% of lead in LCSP sediments is supplied from urban atmospheric pollution. By contrast, human impact in the watershed of Lago Puyehue is very limited. We observe no change in organic geochemistry during the last 150 years and lead contamination remains lower than 5%, even during the last decades. Although contamination levels are much higher in LCSP than in Lago Puyehue, a peak in anthropogenic Pb is recorded during the same period (1974–1976) at both sites. This maximum contamination level is consistent with increased industrial activity in the vicinity of Concepción. Copyright © 2010 John Wiley & Sons, Ltd.



Supporting information may be found in the online version of this article.

KEYWORDS: anthropogenic activity; geochemistry; lead isotopes; lake sediment; Chile.

Introduction

Lake sediments constitute sensitive archives of environmental changes affecting the lakes and their catchments (e.g. Smol, 2008). Since geochemistry of lake sediments is largely controlled by the nature and the processes occurring in the lake catchment (Mackereth, 1966; Engstrom and Wright, 1984), sedimentary geochemistry is one of the best methods to reconstruct palaeoenvironmental changes that occurred in lake watersheds. Moreover, recent improvements in dating techniques (e.g. ^{210}Pb , ^{14}C) of recent sediments allow sediment cores to be used as faithful recorders of recent human

impacts (Smol, 2008). For instance, variations in sedimentation rates have been used to study historical changes in erosion processes and assess land use changes during historical times (Debels *et al.*, 1999; Luque and Julia, 2002). Palaeolimnological approaches have also been used to support studies of identification of metal pollution in aquatic environments (Smol, 2008). Among metals, lead is a good pollution indicator that is immobile in natural environment archives such as lake sediments (Bränvall *et al.*, 2001). Recently, stable Pb isotopic signatures of lake sediments have been used to trace the source of anthropogenic contaminations associated with Pb (e.g. Gallon *et al.*, 2005; Hou *et al.*, 2006; Couillard *et al.*, 2008).

Carbon to nitrogen elemental ratios, as well as stable carbon ($\delta^{13}\text{C}$) or nitrogen ($\delta^{15}\text{N}$) isotope ratios of sedimentary organic matter, are frequently used to reconstruct sources of sedimentary organic matter and past lake productivity (e.g. Schelske and Hodell, 1991; Brenner *et al.*, 1999; Meyers, 2003; Perdue and

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Koprivnjak, 2007; Das *et al.*, 2008). Organic geochemistry reflects the autochthonous or allochthonous origin of the organic matter, i.e., aquatic-derived organic matter vs. terrestrial vegetation. Since terrestrial plants are characterised by C-rich and protein-poor structural material, their C/N atomic ratio is generally well above 20 (Meyers and Terranes, 2001). On the contrary, the C/N ratio of lake plankton averages 8–10, which makes the C/N ratio of lake sedimentary organic matter a useful tool to reconstruct organic matter origin, and environmental changes that occurred in lakes and their watersheds. Similarly, the carbon isotopic composition of organic matter in lake sediments is influenced by both organic matter sources and palaeoproductivity rates (Meyers and Terranes, 2001). Therefore combining organic geochemical composition and stable carbon or nitrogen isotopic signature of lake sedimentary organic matter generally reveals important clues about past lake productivity and changes in terrestrial supplies.

Lead isotope analysis has been applied to diverse materials in order to assess spatial and temporal changes of recent pollution from industries and from leaded gasoline (e.g. Shirahata *et al.*, 1980; Rosman *et al.*, 1993; Véron and Church, 1997). The sources of lead preserved in sedimentary archives are diverse and can be traced using their isotopic signature (Renberg *et al.*, 2002), which depends on the geological origin and age of the original lead-bearing rocks and sediments (Faure, 1986). Naturally, lead is transported to sedimentary environments through weathering of soils and bedrock or more directly within mineral matter eroded from the catchment. The anthropogenic source of lead is associated with airborne particles from leaded gasoline and industries. Alkyl-lead, a common man-made organic form of lead, has been used as a fuel additive to reduce 'knock' in combustion engines since the 1920s (Bollhöfer and Rosman, 2000). Other major sources of atmospheric Pb are mining, smelting, refining of non-ferrous metal, waste incineration and coal burning (Nriagu and Pacyna, 1988; Bollhöfer and Rosman, 2000). Lead is also associated with the emission of other pollutants and it has been used to study long-range transport and atmospheric mixing processes responsible for the pollution of remote environments (e.g., Duce *et al.*, 1983).

Prior to the advent of lead pollution, atmospheric deposition contributed an insignificant fraction of lead accumulated in lake sediments relative to the supply from the catchment (Bindler *et al.*, 2001). However, since ancient times, lead derived from a variety of human activities has been transported atmospherically and deposited on lakes and their catchments (Renberg *et al.*, 2002). In modern times, anthropogenic lead accounts for approximately 95% of the global lead cycle (Settle and Patterson, 1980). On a global scale, ~85% of industrial Pb emissions are introduced in the atmosphere in the Northern Hemisphere (Schaule and Patterson, 1981). Taking into account the residence time of Pb-rich aerosols in the atmosphere (ca 10 days; Settle and Patterson, 1991), those Northern Hemisphere emissions have a negligible impact on the Southern Hemisphere (Bollhöfer and Rosman, 2000).

Early studies of atmospheric contamination of lake sediments focused on long-established industrialised regions of Europe and North America (Boyle, 2001). More recently, work has been undertaken in the newly industrialised countries and in areas less directly influenced by industrial activities. However, the Southern Hemisphere remains relatively understudied. Here, we use stable lead isotopes (new data) and organic geochemistry (new data and data from Bertrand *et al.*, 2005) to identify the environmental impacts associated with increasing industrial activities and land degradation during the last 150 years in south-central Chile. We compare sedimentary

geochemical records from two contrasting lake settings, i.e. Laguna Chica de San Pedro, which is located in an urbanised area and thus immediately affected by pollution, and Lago Puyehue, which is located in an Andean national park with very limited human activities. Our aim is to investigate the local and global impacts of anthropogenic activities in Chile, i.e. one of the most industrialised countries in South America, with over 90% of its population living in urban areas.

Material and study area

Location

Laguna Chica de San Pedro (LCSP; 36° 51' S, 73° 05' W) is a mesotrophic coastal lake located in the vicinity of Concepción, at approximately 3.5 km from the Pacific Ocean (Fig. 1). It is situated in an industrial and highly populated region (population density is 32× the Chilean average), at an altitude of 5 m above sea level (a.s.l.). The bathymetry of the lake is rather simple, with a single basin that reaches a maximum depth of 18 m in its centre (Urrutia *et al.*, 2000a). LCSP presents a surface area of 0.82 km² and a small drainage basin of 4.5 km² (Urrutia *et al.*, 2000a; Parra *et al.*, 2003), which belongs to the metamorphic mountain range of Nahuelbuta. LCSP is surrounded by mountains of Precambrian metamorphic rocks (shale, phyllite) on its eastern side and by Late Pleistocene and Holocene fluvial sandy sediments on its western side (Acencio, 1994; Chirinos, 2005). The watershed of LCSP is a narrow basin, elongated in a north–south direction with steep western and eastern flanks (Debels *et al.*, 1999). It is covered by alfisols (soils developed under temperate forests), which are characterised by a clayey matrix with some quartz grains (Cisternas, 2000). Only one small river drains the watershed of LCSP, and flows into the lake in its southern part. Since the late 19th century, human activities have affected the lake and its watershed through clear-cutting of the native forest, wheat growing, introduction of exotic trees and urbanisation (Cisternas *et al.*, 1999). The native forest occupied 70% of the lake watershed in 1943, and decreased to 13% in 1994. The introduction of the macrophyte *Egeria densa* in the mid 1980s has created apparent oligotrophic conditions (Urrutia *et al.*, 2000b).

Lago Puyehue (40° 40' S, 72° 20' W) is an oligotrophic, moraine-dammed lake located at the foothill of the Cordillera de Los Andes, at approximately 50 km from the city of Osorno (Fig. 1). The lake lies at an elevation of 185 m a.s.l. and has a complex bathymetry, with several sub-basins separated by a continuous bathymetric ridge and with a series of small bedrock islands in its centre (Charlet *et al.*, 2008). The lake has a surface area of 164 km² and a maximum depth of 123 m, and is located in a Tertiary valley over-deepened by Quaternary glacial advances (Campos *et al.*, 1989). The watershed of the lake covers 1267 km² and is composed of Quaternary volcanic rocks that are generally buried under several metres of postglacial andosols (i.e. *Trumaos*) (Laugenie, 1982; Bertrand and Fagel, 2008). Several active volcanoes surround the lake: the Antillanca and Puyehue-Cordón de Caulle volcanic complexes eastward, and the Osorno volcano to the south (Fig. 1). The eastern part of the lake watershed belongs to a natural park (the *Parque Nacional Puyehue*) that is virtually free of anthropogenic influence. The population is concentrated in small low-populated villages along the southern shore of the lake. The whole region is dominated by westerly winds and the lake is fed by Río Golgol to the east

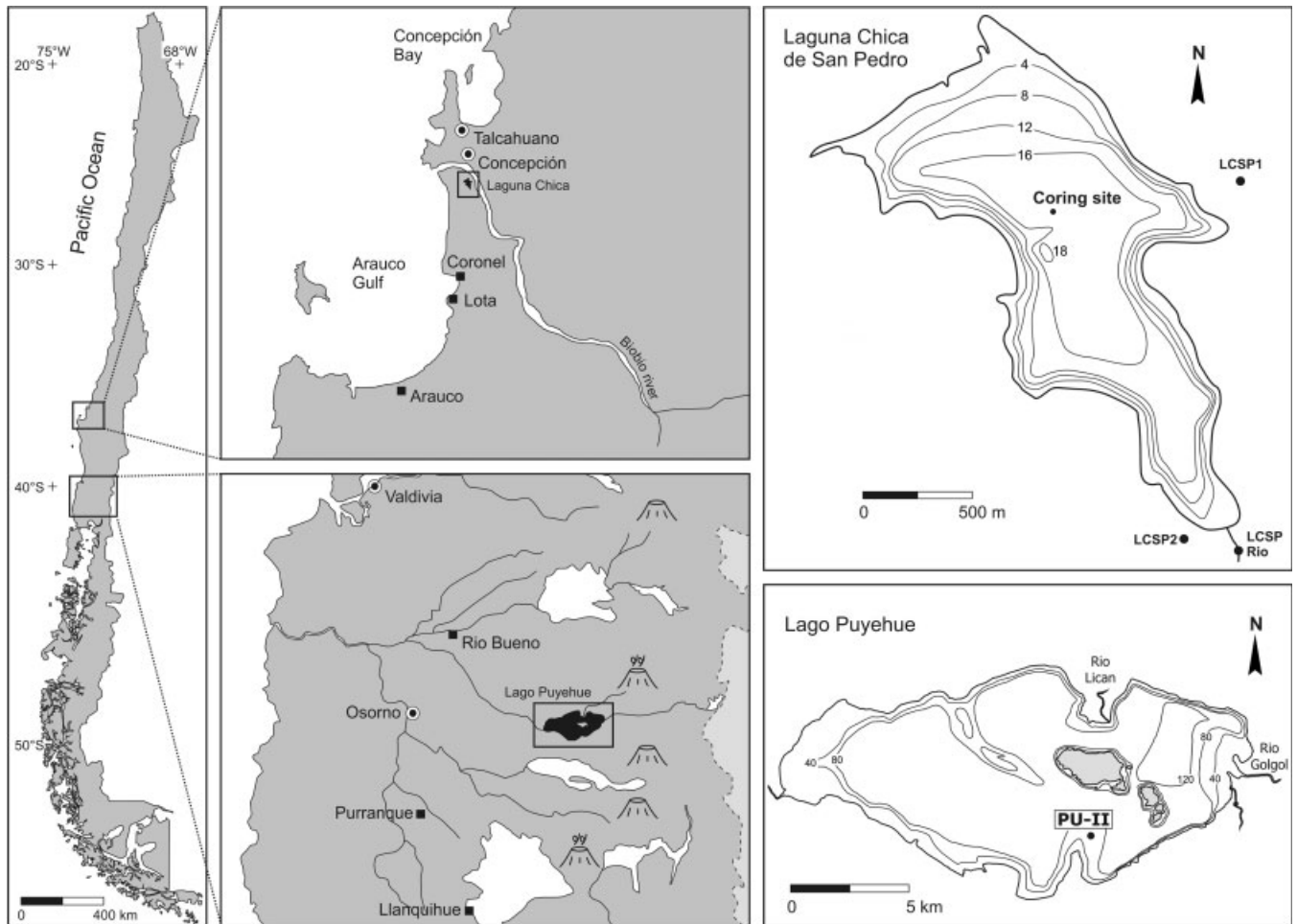


Figure 1 Location of Laguna Chica de San Pedro (LCSP) and Lago Puyehue in south-central Chile. Bathymetric maps are from Campos *et al.*, 1989 (Puyehue) and Urrutia *et al.*, 2000a (LCSP). LCSP1 and 2 indicate the location of the soil samples collected in the watershed of LCSP

and by several smaller rivers (Fig. 1). Its outlet, i.e. Río Pilmaiquen, merges with Río Bueno and flows into the Pacific westward. Since 1944, Río Pilmaiquen has been dammed by a hydro-electric station 6 km downstream of Lago Puyehue (Laugenie, 1982). The lake is monomictic, with stratification in summer and mixing during the winter months (Campos *et al.*, 1989).

Coring and core processing

In May 2003 duplicate sediment cores were taken in the central part of LCSP, at a depth of 17 m (Chirinos *et al.*, 2005b). The sampling site was selected with the aid of a Lowrance X-16 sonar and sediment cores were obtained by divers using 1 m long Plexiglas tubes with an inner diameter of 5.8 cm. The sediment cores were then capped, sealed and stored at 4°C until analysis. For this work, one of the cores has been sampled in 1 cm thick slices. The core is 60 cm long and is composed of dark silty mud containing less than 5% of sand particles (Chirinos *et al.*, 2005b). The sediment is dominated by detrital minerals (clays, plagioclase and quartz) with only a few diatoms (biogenic silica ~3–4%). Microscopically, the sediment is homogeneous without any laminations.

In Lago Puyehue, the selection of the coring site is based on high-resolution seismic profiles obtained in February 2002 (Charlet *et al.*, 2008). Site PU-II is located on a sub-aquatic

moraine ridge at 48.4 m depth in the southern part of the lake (Fig. 1). The site is under the influence of interflows from Río Golgol. At PU-II site, five short cores were taken using a Uwitec short gravity coring device. For this paper, core PU-II-P4 has been opened, described and sampled every 1 cm. Organic geochemistry was measured on parallel core PU-II-P5. Macroscopically, sediment core PU-II-P4 is composed of homogeneous to finely laminated silty sediments, and contains a few tephra layers. The core contains two fine green layers representing the *in situ* alteration of pumices at 4.0–4.5 cm and at 8.5–9.0 cm, and two sandy tephra layers at 12.0–12.5 cm and 42.0–42.2 cm (Bertrand *et al.*, 2005, 2008). Microscopic observations reveal the occurrence of annually laminated sediments composed of an alternation of terrigenous clays and diatomaceous clays, except for a massive layer between 3.5 and 6 cm (Boës and Fagel, 2008).

In addition to the sediment cores, soil and river sediment samples were collected in the watersheds of both lakes. In the watershed of LCSP, we sampled two soil profiles, as well as the sediment of the only river flowing into the lake (Fig. 1). In the watershed of Lago Puyehue, we collected 21 river sediment samples and 12 soil sediment samples from two distinct profiles. The results obtained on these samples are detailed in Bertrand *et al.* (2010). In both cases, the samples have been sieved at 105 µm and the fine fraction of the sediment has been analysed for bulk organic geochemistry according to the methods described hereafter. Some of these samples have also been analysed for lead isotopes (see Tables 3a and 3b, online supporting information).

Chronology

The age–depth model of LCSP sediment core (Fig. 2) is based on ^{210}Pb concentrations (Chirinos *et al.*, 2005a). Ages have been estimated using the constant rate of supply model (CRS) and are listed in Table 2a (online supporting information). The oldest available ^{210}Pb date corresponds to AD 1880 \pm 26, at a depth of 18 cm. Here, we focus on the upper 20 cm of the sediment core, which represents the last ca 150 years. Low sedimentation rates have been calculated between 14 and 18 cm (as low as 0.04 mm a $^{-1}$), and the highest sedimentation rates occur at 9–10 cm (1.5 mm a $^{-1}$, AD 1976–1977).

For the sediments of PU-II coring site, the age–depth model (Fig. 2) is based on varve-counting results obtained on parallel core PU-II-P5 (Boës and Fagel, 2008). They are in agreement with radionuclide profiles (^{210}Pb and ^{137}Cs ; Arnaud *et al.*, 2006) and with the recognition of historically documented event deposits (Bertrand *et al.*, 2008; Boës and Fagel, 2008). In particular, the massive layer microscopically described at 3.5–6 cm has been attributed to the 1960 Valdivia earthquake and used as a time marker (Boës and Fagel, 2008). In this paper, we focus on the upper 22 cm of PU-II-P4 sediment core, which covers the last ca 150 years (AD 1833–1842 at 21.5 cm). Sedimentation rates vary from 0.7 to 1.7 mm a $^{-1}$ (Table 2b, online supporting information).

Methods

Bulk organic geochemistry

Stable isotope ratios of carbon and nitrogen were measured by continuous-flow isotope ratio mass spectrometry after sample combustion to CO_2 and N_2 at 1000°C in an online elemental analyser. For PU-II-P5 sediments, ~25 mg of sediment was

oven-dried, ground and homogenised in an agate mortar, and analysed on a Fisons NA 1500 NC elemental analyser in line with an Optima mass spectrometer (GV Instruments, Lab. Océanologie, University of Liège (ULg), Belgium). The other samples (LCSP, river and soils samples) were freeze-dried, ground and homogenised in an agate mortar, decarbonated using 1N sulphurous acid and analysed at the University of California, Davis (UCDavis) Stable Isotope Facility, USA, on an Europa Hydra 20/20 mass spectrometer in line with an ANCA-GSL elemental analyser. Before introduction to the isotope-ratio mass spectrometer the gases were separated on a Carbosieve G column. Isotopic measurements are presented as δ values (‰) expressed relative to VPDB ($\delta^{13}\text{C}$) or AIR ($\delta^{15}\text{N}$) standards. The precision is calculated by replicate analysis of internal standards, i.e. sucrose (ULg, $\delta^{13}\text{C} = -10.3 \pm 0.2\text{‰}$) or a mixture of ammonium sulphate and sucrose (UCDavis, $\delta^{13}\text{C} = -23.83\text{‰}$, $\delta^{15}\text{N} = 1.33\text{‰}$). For $\delta^{13}\text{C}$, the precision is 0.04‰ (UCDavis) or 0.20‰ (ULg), and the precision for $\delta^{15}\text{N}$ is 0.18‰ (UCDavis).

Inorganic geochemistry and Pb isotopes

Total Pb and Ti concentrations of LCSP sediments were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES) with an accuracy of 16% for Pb and 1.5% for Ti (2 relative standard deviations; Chirinos *et al.*, 2005b). For sediment core PU-II-P4, total Ti concentrations were determined by XRF on fused glass beads, with an accuracy of 3% (Bertrand *et al.*, 2005) and total Pb was estimated by multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS; accuracy 10%).

For Pb isotopes, ~500 mg of sediment was heated at 550°C overnight to volatilise organic matter. The weight loss-on-ignition at 550°C ranges between 13% and 16% for LCSP sediments (Chirinos, 2005) and varies between 1.5% and 11%

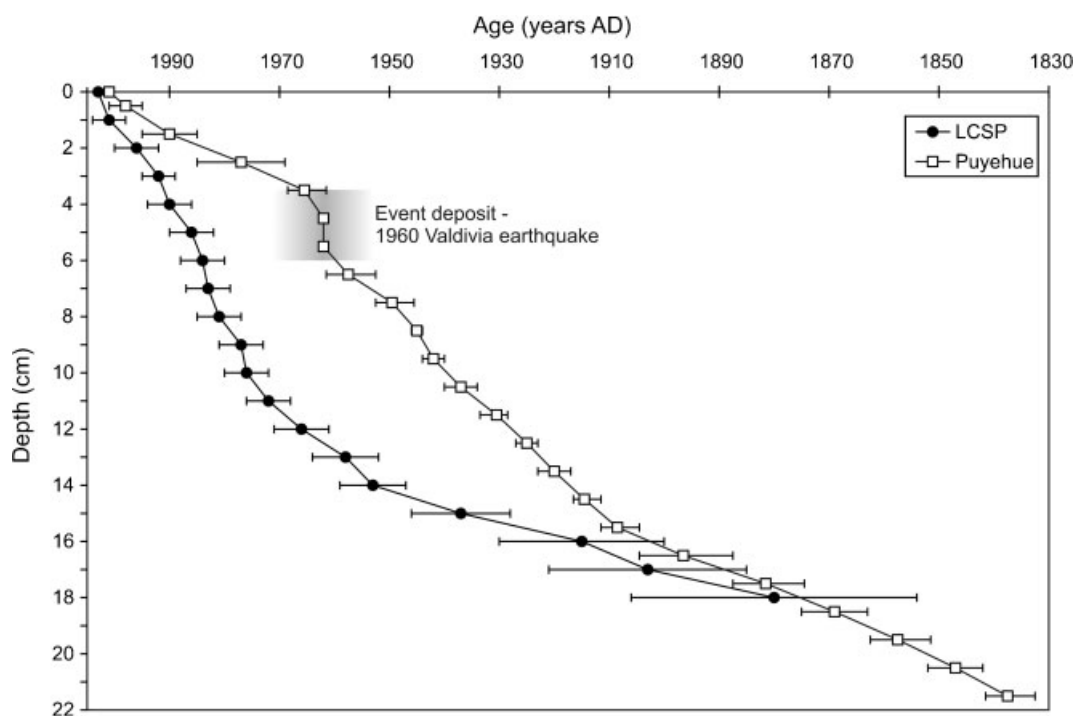
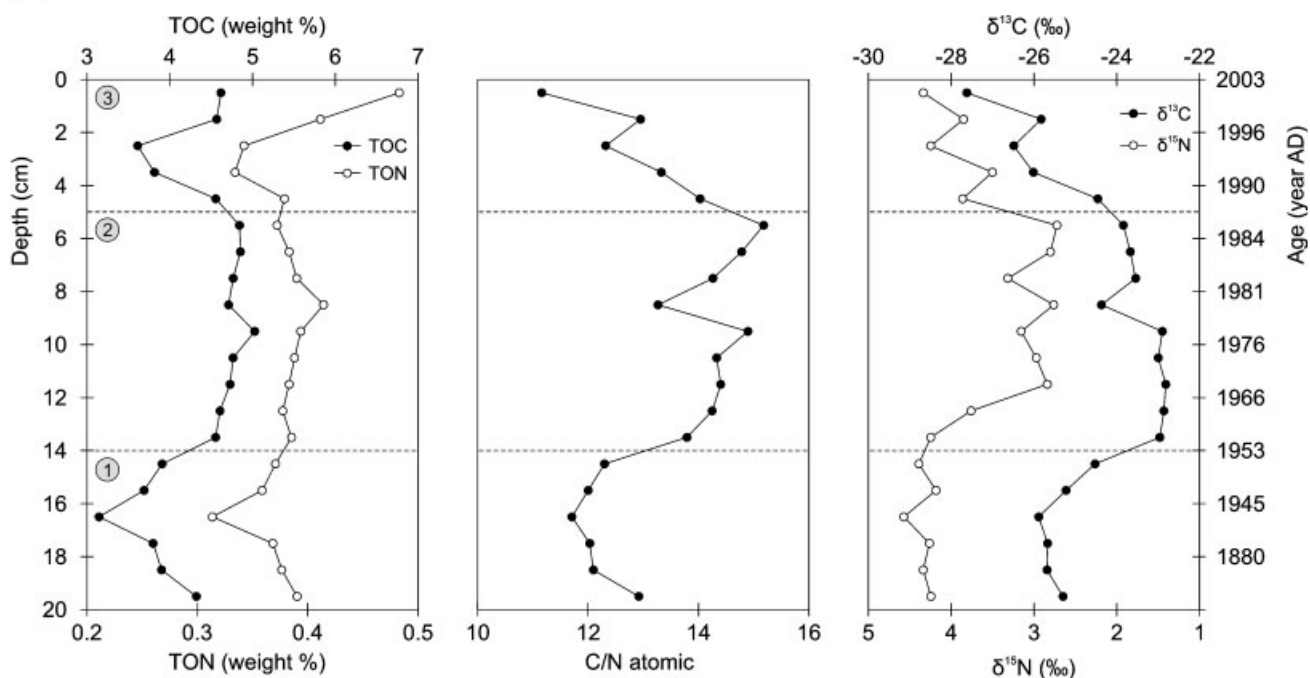


Figure 2 Age–depth models of cores LCSP and PU-II-P4, based on ^{210}Pb analysis (LCSP, data from Chirinos *et al.*, 2005a) and varve-counting (PU-II-P4, data from Boës and Fagel, 2008). For Puyehue, the open squares represent the average age of the 1 cm thick sediment samples used in this study and the error bars are calculated as the cumulated varve-number difference between three independent counts

for PU-II-P4 sediments (Bertrand *et al.*, 2005). The samples (~50 mg for LCSP and 100 mg for PU-II-P4) were subsequently dissolved in closed Teflon beakers in an HF-HNO₃ mixture, and placed on a hotplate (110°C) for 3 days. The solution was then evaporated to dryness, redissolved in HCl, re-evaporated and finally dissolved in 0.8N HBr. Lead (Pb) was chemically extracted using an AG1-X8 anionic resin loaded in a 2 mL column in an HBr environment (Manhès *et al.*, 1978). Pb isotopes were measured by MC-ICP-MS using a Nu-Plasma instrument at the Département des Sciences de la Terre et de

l'Environnement (DSTE, Université Libre de Bruxelles). As an internal isotopic standard, a thallium solution was added to each sample and standard to monitor and correct for mass-dependent isotopic fractionation. While the samples were characterised by a large variability in Pb concentrations, the sample solutions were prepared to obtain a beam intensity in the Axial collector (²⁰⁴Pb) of minimum 100mV, and a Tl/Pb ratio of ~0.2, matching the Pb and Tl concentrations of the NBS981 standard (200 ppb in Pb, added with 50 ppb in Tl). Tl/Pb ratio was relatively stable from one day of analysis to

(a) Laguna Chica de San Pedro



(b) Lago Puyehue

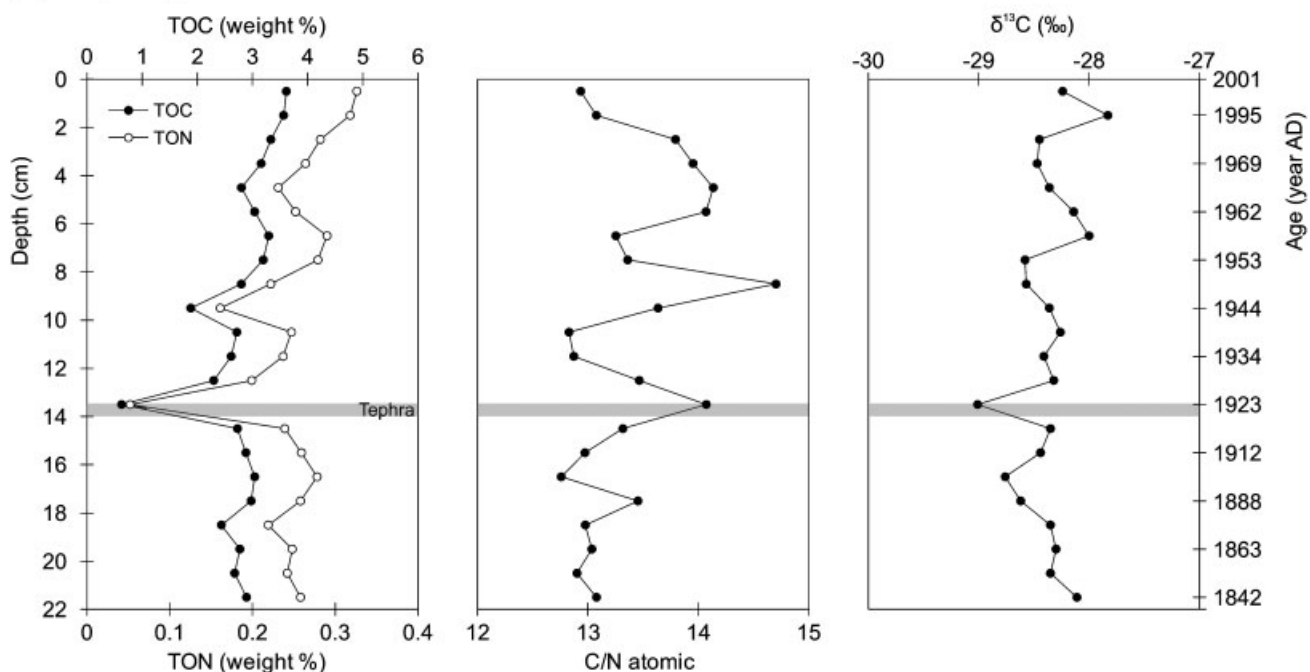


Figure 3 Bulk organic geochemistry of cores LCSP (a) and PU-II-P4 (b). Total organic carbon (TOC) and total organic nitrogen (TON) are in weight %, and δ¹³C and δ¹⁵N are in ‰ relative to VPDB and AIR, respectively. Zones 1, 2 and 3 (LCSP) indicate changes in bulk organic geochemistry, resulting from anthropogenic activities in the lake watershed (see text). Data are presented in Tables 1a and 1b (online supporting information)

another. For PU-II-P4 sediments, TI/Pb ranged between 0.14 and 0.23. For LCSP, this ratio was usually less than 0.5, except for one sample (0.58). Over the course of the study, measurements of NBS981 yielded weighted average values of 36.7158 ± 0.027 (2σ) for $^{208}\text{Pb}/^{204}\text{Pb}$, 15.4969 ± 0.011 for $^{207}\text{Pb}/^{204}\text{Pb}$, 16.9399 ± 0.0011 for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.9148 ± 0.0001 for $^{207}\text{Pb}/^{206}\text{Pb}$, and 2.1674 ± 0.0007 for $^{208}\text{Pb}/^{206}\text{Pb}$, which are in good agreement with long-term laboratory values ($n=1000$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.7130 \pm 0.012$ (2σ), $^{207}\text{Pb}/^{204}\text{Pb} = 15.4950 \pm 0.004$ (2σ), $^{206}\text{Pb}/^{204}\text{Pb} = 16.9393 \pm 0.0044$ (2σ), with the thermal ionisation mass spectrometry (TIMS) values published by Galer and Abouchami (1998), and with the MC-ICP-MS values of Weis *et al.* (2006). These values are also in agreement with TIMS triple-spike values previously published by Galer and Abouchami (1998). Although the NBS981 standard results were within error of the triple-spike values after online correction for instrumental mass bias by TI addition, the results were further corrected by the sample–standard bracketing method (as described by White *et al.*, 2000, and Weis *et al.*, 2006) to circumvent any instrumental drift during the analytical session. Duplicates of the entire analytical procedure ($n=7$) are reported in Table 3 (online supporting information), and all fall within error bars.

Results

Laguna Chica de San Pedro

The total organic carbon (TOC) and total organic nitrogen (TON) profiles of LCSP are roughly parallel, with the TOC and TON values ranging from 3.1% to 5.0% and from 0.3% to 0.5%, respectively (Fig. 3(a)). The C/N atomic ratio varies from 11.2 to 15.2. The carbon and nitrogen isotopic values ranges from -22.8‰ to -27.6‰ and from 2.7‰ to 4.6 ‰, respectively. Two significant changes are observed in all the variables at around 5 cm and 14 cm depth (Fig. 3(a)). The samples collected in the lake watershed show values typical for terrestrial organic matter (C/N: 16.5 ± 1.0 ; $\delta^{13}\text{C}$: -25.8 ± 0.9 ; $\delta^{15}\text{N}$: 7.6 ± 2.5), with no significant difference between the river sediment sample and the soil samples (Table 1a, online supporting information).

Lead concentration and isotopic composition have been determined in 13 samples from LCSP sediment core and on a few samples from the catchment (soil profiles and river sediments; see location on Fig. 1) (Figs 4–6; Tables 2a and 3a, online supporting information). The Pb composition of LCSP sediments remains relatively stable in the lower core

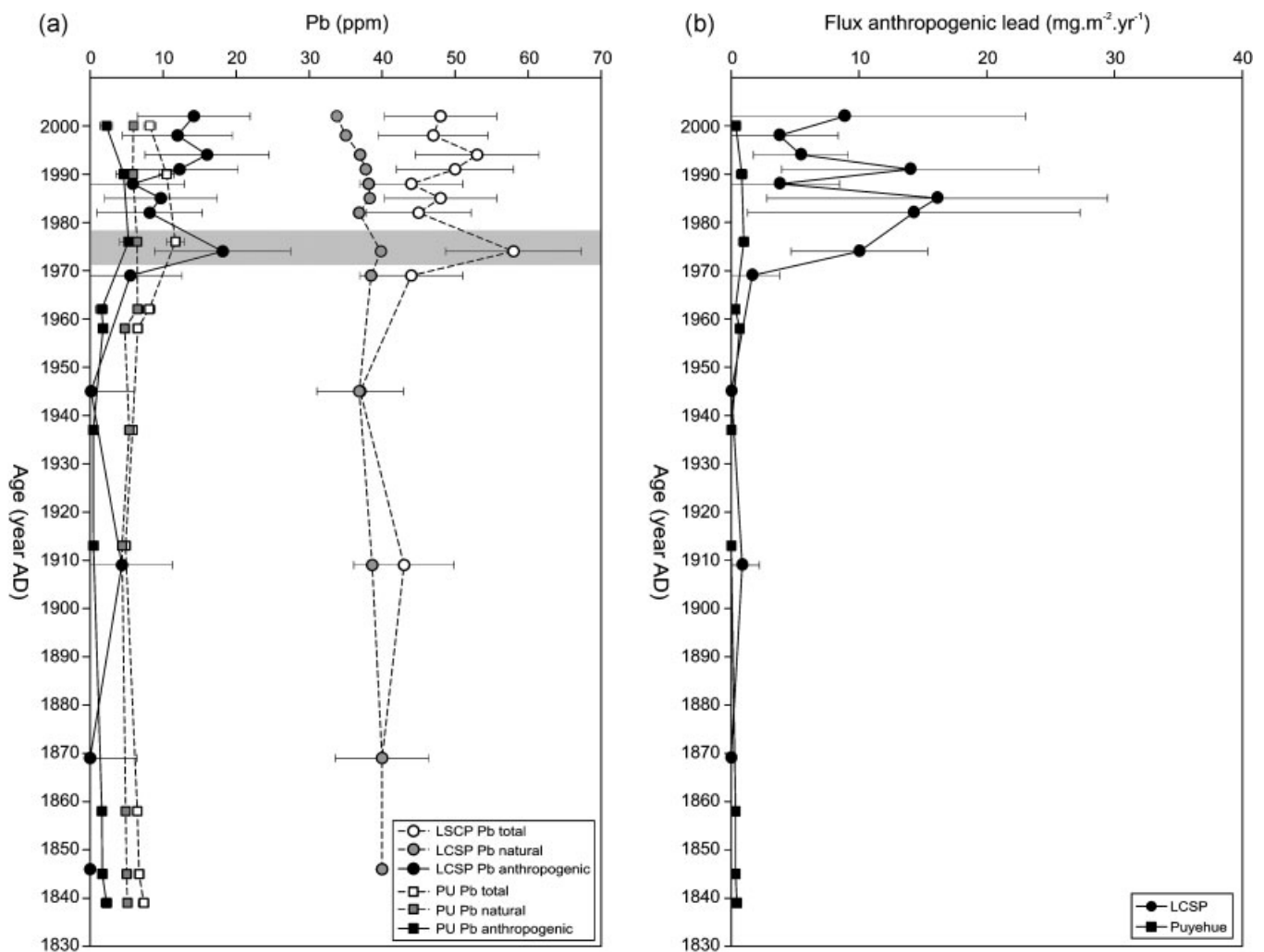


Figure 4 Total, natural and anthropogenic lead concentrations (a), and flux of anthropogenic Pb (b) in sediment cores LCSP and PU-II-P4. In (a), the error bars cumulate errors associated with the geochemical analysis of Pb ($\pm 10\%$ for PU-II-P4, $\pm 16\%$ for LCSP) and Ti (3% for PU-II-P4 and 1.5% for LCSP). In (b), the error bars cumulate the errors on anthropogenic lead concentrations, sediment accumulation rates and density. See online supporting information for data

section, i.e. in the interval between 11 and 20 cm corresponding to sediments older than AD 1972 (Fig. 5). For instance, the mean $^{206}\text{Pb}/^{204}\text{Pb}$ ranges around 18.533 ± 0.022 (2σ). Then a shift to lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios is observed in the upper 10 cm (Figs 5 and 6). It is especially pronounced in the last 3 cm, i.e. in sediments younger than 1992 (Fig. 5). The $^{206}\text{Pb}/^{204}\text{Pb}$ ratio decreases down to 18.257 ± 0.022 in the upper 0–1 cm sample. The range of variation in $^{206}\text{Pb}/^{204}\text{Pb}$ ratio ($\sigma = 0.079$) reached in the upper section is fourfold higher than in the lower section. Note that the general trend in the Pb isotopic profile, in particular the uppermost sharp shift, is confirmed by the three duplicate analyses reported in Fig. 5. The signature of the soil and river samples is more scattered, with $^{206}\text{Pb}/^{204}\text{Pb}$ ranging between 18.481 and 18.768 (mean = 18.628; $\sigma = 0.11$; online supporting information Table 3a). The river sediments and the lower soil sample of site 2 display the highest isotopic ratios. The lowest isotopic ratios (e.g. $^{206}\text{Pb}/^{204}\text{Pb} = 18.4807 \pm 0.0010$) are recorded in the upper soil sample at site 2 (see Fig. 1 for location). At site 1 the two soil samples collected from the upper brown to black and lower red to brown horizons give similar Pb composition (e.g. $18.5847 \pm 0.0009 < ^{206}\text{Pb}/^{204}\text{Pb} < 18.5869 \pm 0.0009$, online supporting information Table 3a). Those Pb ratios are more radiogenic than the lacustrine sediments values. For instance, all the $^{206}\text{Pb}/^{204}\text{Pb}$ values for

LCSP are lower than 18.5644 ± 0.0018 . The mean soil signature displays slightly more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (18.593) than the lower core section (Fig. 5).

Lago Puyehue

The TOC and TON profiles of the upper 22 cm of PU-II-P5 sediment core are roughly parallel (Fig. 3(b)), with particularly low values at 13.5 cm, which are due to the occurrence of a tephra layer (Bertrand *et al.*, 2005). The lake sediments (excluding the tephra layer) are characterised by TOC and TON values ranging from 1.9% to 3.6%, and from 0.3% to 0.2%, respectively, and slightly decreasing towards the bottom of the core. The C/N ratio and the $\delta^{13}\text{C}$ values do not show any particular trend, and the values range between 12.8 and 14.7 for C/N and between -27.8‰ and -28.8‰ for $\delta^{13}\text{C}$. The river sediment samples are characterised by more terrestrial values that do not vary significantly between the different rivers (C/N: 13.1 ± 1.0 and $\delta^{13}\text{C}$: $-27.2\text{‰} \pm 0.5\text{‰}$). Details regarding each particular river are given in Bertrand *et al.* (2010).

The Pb elemental and isotopic composition of 10 bulk sediment samples from sediment core PU-II-P4 are reported in Figs 4,5 and 6, and the data are presented in Tables 2b and 3b (online supporting information). The Pb isotopic ratios vary within a narrow range in most of the studied core section. For instance, the $^{206}\text{Pb}/^{204}\text{Pb}$ values are comprised between 18.5069 ± 0.0007 and 18.6097 ± 0.0008 (Fig. 5). Similarly to the LCSP record, a slight excursion to lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios occurs in the upper sediment section. The change is gradual. It appears within the upper 3 cm, i.e. since at least AD 1976 (Fig. 5). Again, duplicates ($n=5$, online supporting information Table 3a) confirmed the observed isotopic trend.

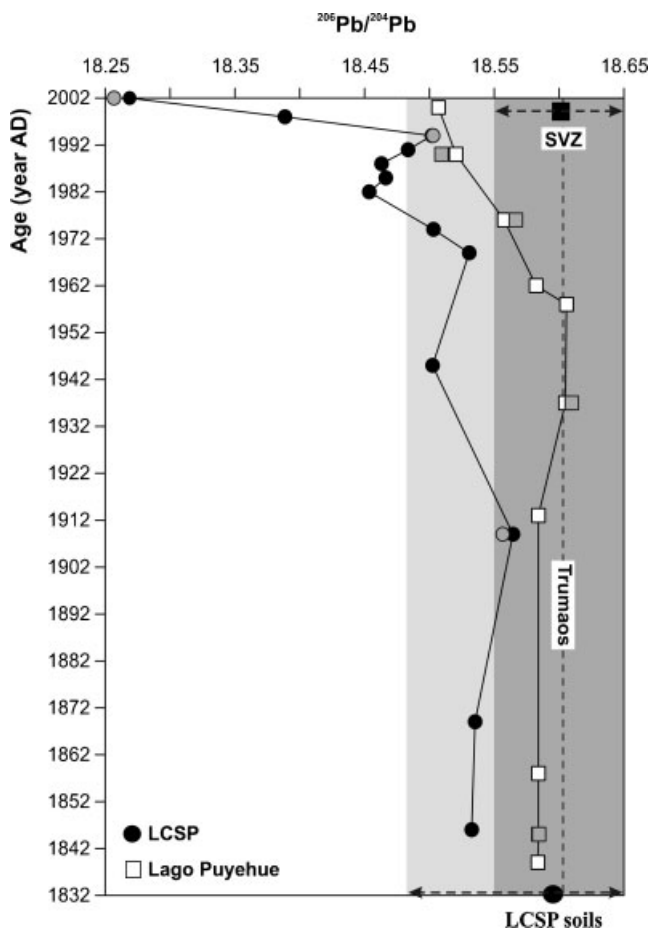


Figure 5 Temporal evolution of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios measured on bulk lake sediments from LCSP and Lago Puyehue. The grey symbols correspond to duplicate analyses. 'SVZ' (upper dashed arrow and dark grey area) refers to the isotopic composition of rocks from the Southern Volcanic Zone of Chile. 'Trumaos' (vertical dashed arrow) refers to the isotopic composition of soils in the vicinity of Puyehue. 'LCSP soils' (lower dashed arrow and light grey area) refers to the mean isotopic composition of soils in the watershed of Laguna Chica de San Pedro. Data are presented in Tables 3a and 3b (online supporting information)

Discussion

Sources of organic matter and land-use changes over the last 150 years

Here, we use the bulk organic geochemical data obtained on the sedimentary organic matter of LCSP and PU-II-P5 to reconstruct the variations in the main sources of organic carbon during the last 150 years. In lake systems, terrestrial plants and lake plankton generally have very similar $\delta^{13}\text{C}$ values (-25‰ to -30‰ for lake plankton, -22‰ to -30‰ for C3 terrestrial plants) but significantly distinct C/N atomic ratios (Meyers and Teranes, 2001). Therefore, our interpretation in terms of sources of sedimentary organic matter is primarily based on the carbon to nitrogen ratio data.

Laguna Chica de San Pedro

In LCSP, the lake sedimentary organic matter represents a mixture of terrestrial organic matter (C/N: 16.5 ± 1.0) and lake plankton (C/N generally between 6 and 10, Meyers and Terranes, 2001). Shifts towards higher C/N ratios are interpreted as a higher supply of terrestrial organic matter and/or lower lake productivity and vice versa. At LCSP, the measured C/N atomic ratios and isotopic values display significant and concomitant shifts, evidencing a variable contribution of lake *versus*

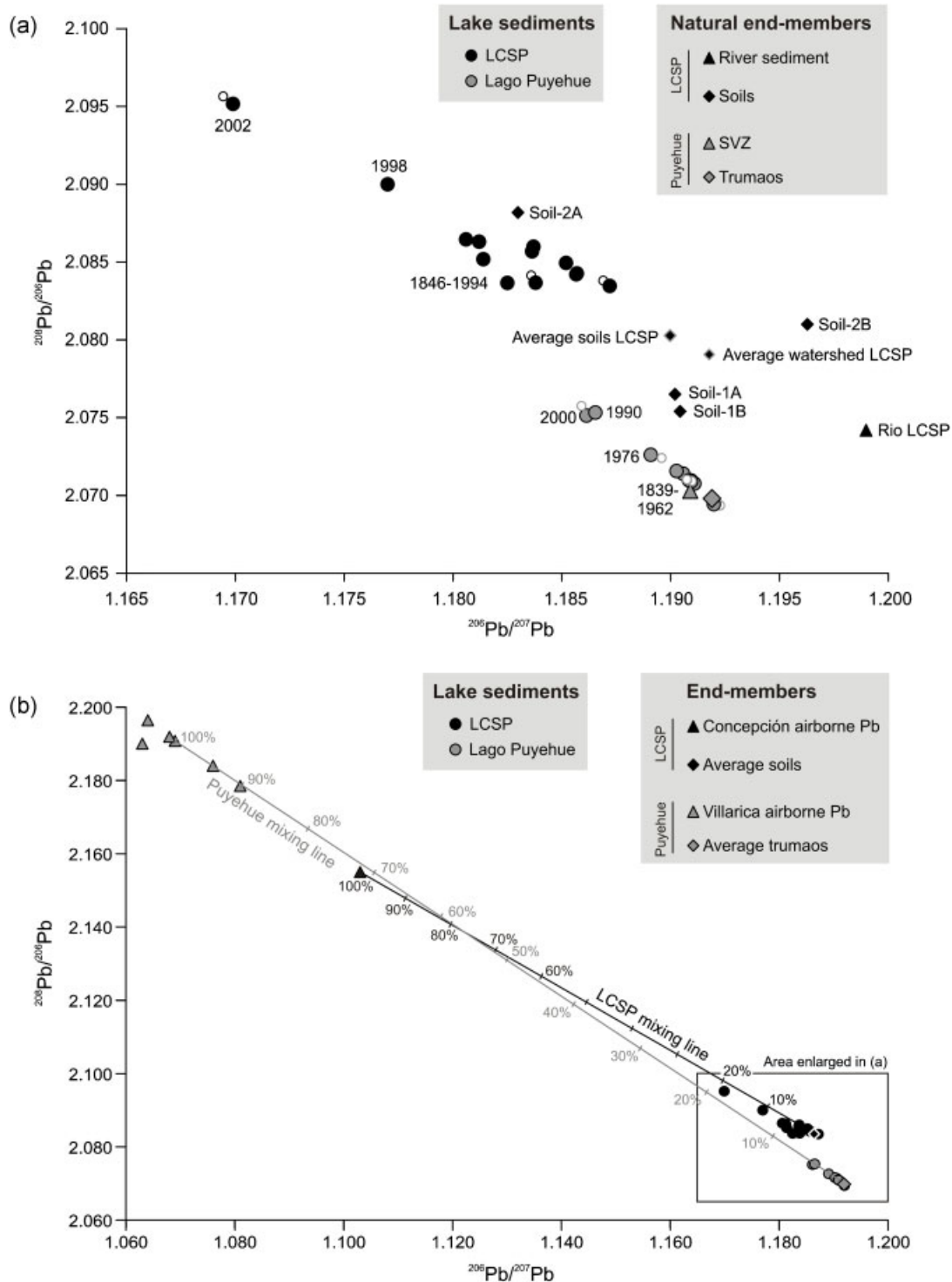


Figure 6 $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic biplots. (a) Close-up on data obtained from lake sediment samples. Open symbols represent duplicate analyses. The values calculated for the natural end-members are also indicated. SVZ, Southern Volcanic Zone. (b) Extended biplot showing the data obtained on the lake sediment samples, selected end-members and mixing lines (with 10% increments). For data and/or references see Tables 3a and 3b (online supporting information)

terrestrial organic matter during the last ~150 years. In the deepest part of the core (20–14 cm, i.e. AD 1880–1953) the C/N ratios are relatively low (~12), evidencing a high contribution of lake plankton compared to the supply of terrestrial organic matter. Then, around 1950–1955, the C/N ratios and the TOC sharply increase, which probably represents a higher supply of terrestrial organic matter, with ~80% of the organic matter originating from the lake watershed. The C/N values remain high until around 1986, where they gradually decrease towards the present-day conditions, reflecting a decrease in the terrestrial supply of sedimentary organic matter and/or higher

lake productivity during the last two decades. During the last 17 years, the TOC values are generally low, evidencing that the shift in the C/N atomic ratio at around 5 cm is most likely due to a decrease in the supply of terrestrial organic matter. A shift towards less negative $\delta^{13}\text{C}$ and a concomitant decrease of the $\delta^{15}\text{N}$ values (Fig. 3) in AD ca 1953 are in agreement with an increased supply of terrestrially derived organic carbon during the AD 1953–1986 period.

The significant increase in the supply of terrestrial organic matter to LCSP at around 1953 is strikingly consistent with a rapid increase in the total mass accumulation rate of sediment

in the same core (Chirinos *et al.*, 2005a) and in another core from the same lake (Cisternas and Araneda, 2001; Cisternas *et al.*, 2001). In addition, Urrutia *et al.* (2000b) observed a significant increase in terrestrial hydrocarbons and fatty acids in ca 1945 in agreement with our interpretation.

The observed changes in the supply of terrestrial organic carbon are most likely linked to anthropogenic activities in the watershed of LCSP, mostly related to deforestation. Although the replacement of the native forest by commercial plantation in the watershed of LCSP began at the end of the 19th century, it only became intensive in the mid 20th century (Debels *et al.*, 1999; Urrutia *et al.*, 2000b; Cisternas *et al.*, 2001). In 1943, the native forest still occupied 70% of the watershed area and no area had been left deforested (Cisternas *et al.*, 2001). Between 1943 and 1955, 17% of the forest had been logged and replaced by exotic species. Most of the native species disappeared between 1943 and 1994 (from 70.1% to 12.6%). Although some of them have been replaced by pine plantations, deforested areas started to occur in 1961, and were covering up to 22% of the lake watershed between 1961 and 1981 (Cisternas *et al.*, 2001). In 1994, most of the watershed had been replanted with exotic species. In the watershed of LCSP, human settlement began in 1961 and peaked in 1981 (Cisternas *et al.*, 2001).

Deforestation and denudation of the soil cover generally result in increased soil erosion and runoff of soil particles (including organic matter), which in turn triggers higher sedimentation rates in lake sediments (e.g. Page and Trustrum, 1997). The increased supply of terrestrial organic matter in the sediments of LCSP between 1953 and 1986 is in good agreement with the peak of anthropogenic activities in the lake watershed, especially deforestation, clear-cutting of indigenous species and human settlement. After 1986, our results show a decrease in TOC and C/N, which reflects a decrease in the supply of terrestrial organic matter into the lake. This change is very likely related to the stabilisation of the soils in the lake watershed in response to reforestation after 1981. It is noteworthy that the anthropogenic introduction of the macrophyte *Egeria densa* in LCSP in the mid 1980s (Urrutia *et al.*, 2000b) is not directly recorded in the lake sediments (i.e. no increase in C/N), although it acted a sink for nutrients, resulting in the actual apparent oligotrophication of the lake.

Lago Puyehue

The sedimentary organic matter of core PU-II-P4 is composed of a mixture of terrestrial and aquatic end-members that are characterised by average C/N atomic ratios of 13.7 (river sediment), 14.6 (soils and palaeosols) and 8.5 (lake plankton), respectively (Bertrand *et al.*, 2010). By contrast with the sediments of LCSP, the sediments of Lago Puyehue show rather stable C/N and $\delta^{13}\text{C}$ values during the last 150 years (Fig. 3), ranging around 13.4 and 28.4‰, respectively. No significant trend is observed and the only excursions of the C/N ratio occur at 8–9 and 13–14 cm, in relation with a clay layer (weathered pumices) and a sandy tephra layer, respectively. Because of the remote location of Lago Puyehue and its situation within a national park, anthropogenic impacts in the lake watershed are very minor, and do not affect the soil erosion and the terrestrial runoff. Neither can they modify the lake trophic conditions. Therefore, the composition of the bulk sedimentary organic matter in Lago Puyehue reflects the natural supply and export production of terrestrial and aquatic organic matter. Changes in its composition over longer timescales are driven by natural

variations in lake productivity, resulting from natural changes in the supply of nutrients to the lake (Bertrand *et al.*, 2005). The sediments of Lago Puyehue are therefore a good archive of palaeoclimate changes over the last millennia (Bertrand *et al.*, 2005) and even since the Last Glacial Maximum (Bertrand *et al.*, 2010), but do not contain any evidence of anthropogenic impact.

Sedimentary Pb isotopes: a record of human activities over the last 150 years

Stable Pb isotopes in lake sediments are widely used in environmental studies as tracers of historical pollution (e.g. Brännvall *et al.*, 1997; Arnaud *et al.*, 2004; Vermillon *et al.*, 2005; Couillard *et al.*, 2008). Lead pollution in lake sediments can be traced using two distinct methods. The first one, generally less accurate than the second, uses lead concentrations. The second method, using lead stable isotopes, is much more precise, and generally allows one to trace the sources of lead. Here, we compare estimates calculated by both methods.

Estimation of anthropogenic lead using Pb concentrations

Lead concentrations in sediments ($\text{Pb}_{\text{sample}}$) integrate both the natural Pb associated with the sediment matrix and the Pb supplied from atmospheric pollution. Therefore, the easiest method to estimate the anthropogenic fraction of Pb ($\text{Pb}_{\text{anthropogenic}}$) in lake sediments is by subtracting the natural Pb concentration from the sample concentration (Fig. 4). To take into account the variations of Pb concentration related to change in sediment composition (i.e. dilution effect), the natural Pb fraction is estimated for each sample by using the sample concentration of a naturally derived conservative element (Arnaud *et al.*, 2004). Assuming that the natural Pb/Ti ratio is constant in the whole core, the anthropogenic Pb concentration is calculated following equation (1):

$$\text{Pb}_{\text{anthropogenic}} = \text{Pb}_{\text{sample}} - [(\text{Ti}_{\text{sample}} * \text{Pb}/\text{Ti}_{\text{natural}})] \quad (1)$$

where $\text{Pb}/\text{Ti}_{\text{natural}}$ is the Pb/Ti ratio measured in pre-anthropogenic sediments.

The assumption that the $\text{Pb}/\text{Ti}_{\text{natural}}$ ratio of pre-anthropogenic sediments is constant in the whole core is usually valid for lakes with catchments characterised by a relatively small size (as for LCSP) and/or by a simple and homogeneous geology (as for both lakes: metamorphic rocks in LCSP, dominant volcanic andesitic or basaltic rocks in Puyehue).

In order to compare distant records, anthropogenic Pb fluxes are generally more appropriate than concentrations (Arnaud *et al.*, 2004). Therefore, we calculated the flux of bulk (F_{bulk}) and anthropogenic ($F_{\text{anthropogenic}}$) lead using the concentration data, the dry density D (g cm^{-3}) and the sediment accumulation rate SAR (cm a^{-1}) estimated from the respective age models:

$$F_{\text{bulk}} = D * \text{SAR} * \text{Pb}_{\text{sample}} \quad (2)$$

$$F_{\text{anthropogenic}} = F_{\text{bulk}} * \% \text{Pb}_{\text{anthropogenic}} \quad (3)$$

For PU-II-P4 sediment samples, the total Pb concentrations are low and vary around 8 p.p.m. (standard deviation: 2 p.p.m.), with slightly higher values after 1962 (Fig. 4). This value is close to the natural background Pb concentrations (7 p.p.m.) in the regional andosols (Deraymaeker, 2003). The calculated $\text{Pb}_{\text{anthropogenic}}$ reaches its maximum (5 p.p.m.) in

the sample corresponding to year 1976, where it represents more than 40% of the total Pb (Fig. 4). This corresponds to the highest anthropogenic flux ($1.0 \text{ mg m}^{-2} \text{ a}^{-1}$).

In LCSP sediments, the total lead concentration increases from 40 p.p.m. in the pre-industrial samples (before 1965) up to a maximum of 58 p.p.m. in the sample corresponding to year 1974 (Fig. 4). This corresponds to 18 p.p.m. of $\text{Pb}_{\text{anthropogenic}}$ and an anthropogenic flux of $10 \text{ mg m}^{-2} \text{ a}^{-1}$. The flux of $\text{Pb}_{\text{anthropogenic}}$ is the highest in 1985 ($16.1 \text{ mg m}^{-2} \text{ a}^{-1}$) but is generally well above $10 \text{ mg m}^{-2} \text{ a}^{-1}$ between 1974 and 1991, where it represents up to 30% of the total Pb.

In both lakes, we evidence a peak in Pb concentration in 1974–1976 (Fig. 4). Taking into account the error in age model and the sampling resolution, this corresponds to a synchronous change despite the contrasted environments of the two lake settings. Such change underlines the global character of Pb contamination in Chile. The contamination by industrial airborne particles is approximately 10 times greater in LCSP than in Lago Puyehue, reflecting the natural setting characterising the region of Puyehue. Interestingly, the inception of airborne pollution in LCSP is consistent with the detection of spheroidal carbonaceous particles (SCP), i.e. residue of fossil fuel combustion, in LCSP sediments. Indeed, using the same sediment core, Chirinos *et al.* (2005a) have detected the occurrence of SCP only in sediments younger than 1976 (first 11 cm of the sediment core). Detection of contamination in newly industrialised countries and in areas remote from industry can be difficult and it is important to pay attention to estimation of the natural concentrations, especially in regions where atmospheric contamination is minor (Boyle, 2001), as is the case in Chile. Even if Concepción is one of the most industrialised cities in Chile, the flux of anthropogenic Pb recorded in the sediments of LCSP ($10\text{--}15 \text{ mg m}^{-2} \text{ a}^{-1}$) is still two to three times lower than in the French Alps and in Canada ($30 \text{ mg m}^{-2} \text{ a}^{-1}$; Arnaud *et al.*, 2004; Ndzangou *et al.*, 2005).

Estimation of anthropogenic lead using Pb stable isotopes

The anthropogenic lead content can similarly be calculated using lead stable isotopes, with the main advantage that we can now discuss the possible sources of anthropogenic lead. The downcore records of the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio are illustrated in Fig. 5. They show that the Pb isotopic composition of the two sedimentary environments depicts a similar trend through the last ca 150 a, with less radiogenic values in the most recent sediments. The isotopic sedimentary Pb signatures are relatively constant in older sediments (Fig. 5). The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ results are illustrated in Fig. 6. At both sites, we note a decrease of the $^{206}\text{Pb}/^{207}\text{Pb}$ and an increase of $^{208}\text{Pb}/^{206}\text{Pb}$ ratios towards the surface (Fig. 6(b)). The shift seems to start earlier in the sediments of LCSP than in those of Lago Puyehue, (i.e. between 1969 and 1976 and between 1976 and 1990, respectively), although this might be affected by the relatively low sampling resolution. These trends evidence a supply of anthropogenic Pb that can be estimated using Pb isotopes after identification of the isotopic signatures of the natural and anthropogenic sources. In both lakes, the lead isotopic compositions ($^{206}\text{Pb}/^{207}\text{Pb} - ^{208}\text{Pb}/^{206}\text{Pb}$) are distributed along two different trends (Fig. 6), which can be interpreted as mixing lines between two end-members. One end-member represents the regional natural background sedimentation. The other end-member, characterised by lower $^{206}\text{Pb}/^{207}\text{Pb}$ and higher $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, coincides with the anthropogenic source.

Identification of the natural sources of lead. In lake sediments the 'old' or pre-industrial samples are usually used as representative of the isotopic composition of the sediment matrix (e.g. Arnaud *et al.*, 2004). In Lago Puyehue, a long record of the sedimentary Pb composition is available (Deraymaeker, 2003). The range of variation of Pb ratios measured on an 11 m long core (PU-II) is narrow. The Holocene and deglacial sediments are characterised by stable Pb isotopic signatures. Their averaged signature ratios ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.191$; $^{208}\text{Pb}/^{206}\text{Pb} \sim 2.071$) are therefore used to characterise the natural end-member. The definition of this natural end-member is consistent with regional soil and volcanic rock data (Fig. 6). The Puyehue catchment is covered by volcanic-derived soils ('Trumaos'; Bertrand and Fagel, 2008), characterised by $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.192 and 2.070, respectively. The Trumaos signature is therefore in good agreement with the sedimentary pre-anthropogenic Pb isotopic composition (Deraymaeker, 2003; Fig. 6). The average Pb isotopic composition of the volcanic rocks from the surrounding area also perfectly agrees with the composition of the pre-industrial sediments. For instance, the mean $^{206}\text{Pb}/^{204}\text{Pb}$ value calculated for the Southern Volcanic Zone (SVZ) between 36° and 41° S (18.5984 ± 0.0619 , online supporting information, Table 3b) perfectly agrees with the sedimentary $^{206}\text{Pb}/^{204}\text{Pb}$ values of PU-II-P4 below 3 cm (Fig. 5). In the $^{208}\text{Pb}/^{206}\text{Pb} - ^{206}\text{Pb}/^{207}\text{Pb}$ biplot (Fig. 6), the mean SVZ signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.192, $^{208}\text{Pb}/^{206}\text{Pb}$: 2.068–2.070) is adjacent to the Trumaos-representative signature.

According to the ^{210}Pb age model, the sediment core from LCSP can be divided into a pre-industrial period before 1915 (below 16 cm) and an industrial period after 1915 (Chirinos *et al.*, 2005b). We can therefore estimate the natural Pb isotopic signature by the averaging the results of the three lowest samples, resulting in $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 1.186 and 2.084, respectively (online supporting information, Table 3a). Unfortunately, there is a lack of data regarding the Pb isotopic composition of rocks in the region of Concepción. However, in January 2007 we collected and analysed several sediment samples from soils outcropping around the lake and from the only river flowing into LCSP. Although we are aware this sampling is not exhaustive, it gives an estimate of the scattering of the natural Pb isotopic composition of the LCSP watershed. The mean watershed signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.192; $^{208}\text{Pb}/^{206}\text{Pb}$: 2.079) and the mean soil signature ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.190; $^{208}\text{Pb}/^{206}\text{Pb}$: 2.080) are comparable to the Pb isotopic composition of the pre-industrial LCSP sediment samples (Fig. 6). The only outlier is soil 2A, which has been collected in the upper part of an outcrop in the southern part of the lake watershed, and may therefore contain industrial lead.

Identification of the anthropogenic sources of lead. The composition of the anthropogenic end-member is influenced by Pb atmospheric emissions related to alkyl-lead and industrial activities. Bollhöfer and Rosman (2000) have analysed aerosols collected between 1994 and 1999 at >70 sites widespread in the Southern Hemisphere in order to define the modern isotopic signature for atmospheric lead. The isotopic composition in Chile is characterised by low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (down to 1.06 at the southern tip of Chile), probably reflecting the supply of alkyl-lead from the UK producer Associated Octel, i.e. the world's primary alkyl-lead producer. Associated Octel has used Pb from different ores (e.g. Broken Hill in Australia) in variable proportions with time and location (Véron *et al.*, 1999). In Chilean airborne samples, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, for instance, increases northward, from Punta Arenas (1.063) via Villarica (1.069) and Concepción (1.103) up to a maximum ratio of 1.150–1.182 in Santiago (see online supporting information,

Table 3). This shift can be explained either by different market shares in petrol (different alkyl-lead mixtures provided to different cities) or by a change in relative contribution of industrial Pb and leaded petrol. Industrial activities may be a more important source of atmospheric Pb in Santiago than at the southern tip of the country. Keeping in mind this spatial variability, we selected the lead isotopic signature of airborne particles from the closest city of each lake (Concepción for LCSP, Villarica for Puyehue) to characterise the anthropogenic end-member of each location.

Estimation of natural vs. anthropogenic lead contribution using Pb isotopes. Assuming that the lead isotopic composition of each sample is a mixture of only two sources, i.e. natural lead derived from soil and rocks from the catchment (IS_{natural}) and anthropogenic lead ($IS_{\text{anthropogenic}}$), we can estimate the relative contribution of natural and anthropogenic lead using a simple binary mixing model (equation 4; e.g. Renberg *et al.*, 2002):

$$IS_{\text{sample}} = \alpha * IS_{\text{anthropogenic}} + \beta * IS_{\text{natural}}, \text{ with } \alpha + \beta = 1 \quad (4)$$

The end-members used in our calculation and the calculated mixing lines are reported in Fig. 6(b). Because of the relatively low precision of the Pb concentration data, the mixing trends could not be verified in an isotope-element mixing diagram (1/Pb concentration vs Pb isotopic composition). In the region of Puyehue the contribution of anthropogenic Pb always remains lower than 5% during the last 150 years (Fig. 6). This low environmental contamination level persists during the late decade. At LCSP, the fraction of anthropogenic Pb significantly increases during recent years (Fig. 6), from less than 5% between 1945 and 1994, to 10% in 1998 and even 20% in 2002 (Fig. 6(b)).

Anthropogenic lead: general interpretation and comparison of the two estimates

Although several studies suggest that the main process of anthropogenic lead incorporation into lake systems is direct atmospheric deposition (Dillon and Evans, 1982; Blais and Kalff, 1993), others show that pollutants previously deposited in lake catchments also contribute significantly to the global supply of Pb to lake sediments (Miller and Friedland, 1994). These studies, however, show that the anthropogenic lead, mainly deposited in lake catchments after 1960, will not be released to upland streams before the middle of the next century (Miller and Friedland, 1994), and has therefore no influence on the lake sedimentary records of Pb pollution. In addition, the recent increase in anthropogenic lead at LCSP can only represent a direct atmospheric supply since the reforestation of the LCSP watershed has stabilised soils and reduced the sediment supply to the lake. Keeping in mind that small variations in concentration may be difficult to interpret (Bränvall *et al.*, 2001), we consider that the anthropogenic estimates using Pb concentrations fit noticeably well with our Pb isotopic approach. Although the estimates using Pb concentrations are constantly higher than the estimates using Pb isotopes, both methods show an increased anthropogenic lead supply for the last 30 years, which is much more distinct in the region of Concepción than around Puyehue.

Summary and conclusion

We used a geochemical approach combining elemental and isotopic carbon, nitrogen and lead, to compare the anthro-

pogenic impact in south-central Chile, as recorded in two contrasted lake settings, i.e. LCSP located near the city of Concepción (36° S) and Lago Puyehue, situated in a National Park at the foothills of the Chilean Andes (40° S).

For the region of Puyehue both methods underline the minimal impact of anthropogenic activities on the natural sedimentation processes. Although the lake receives a small amount of anthropogenic lead from atmospheric deposition, its relative contribution is always lower than 5%. Since no industrial activity takes place in the watershed of the lake, the anthropogenic lead deposited in Lago Puyehue probably originates from relatively long-distance atmospheric transport. A fraction of the Puyehue anthropogenic lead may also originate from road transport to Argentina, as one of the main routes to cross the Andes runs along the southern shore of the lake.

Recent sedimentation in LCSP reflects variable human activities in the region of Concepción during the 20th century. The bulk organic geochemical data provide clear evidence for deforestation episodes in the lake watershed from 1915–1937 to the late 1980s, with an accentuation between 1943 and 1987, when most of the native forest was logged and replaced by exotic species. Using two different approaches, we demonstrate that airborne pollution in the region of Concepción started to become significant some time between 1974 and 1982. We estimate that anthropogenic lead constitutes up to 10–20% of total Pb supplies during the last decade. This interpretation is consistent with the detection of spheroidal carbonaceous particles, i.e. residue of fossil fuel combustion, in lake sediments deposited after 1976.

Although the contamination levels are much higher around Concepción than in the region of Puyehue (the Pb anthropogenic flux is 10 times lower at Puyehue than at LCSP), maximum Pb contamination is observed in the mid 1970s (1974–1976) at both sites, suggesting a large-scale Pb pollution.

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